OFFICE OF NAVAL RESEARCH

Contract N00014-91-J-1758

R&T Code 4135026---01

Technical Report No. 3

Luminescent Nitro Derivatives of Benzotriazolo[2,1-a]benzotriazole

by

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Submitted to

Heteroatom Chemistry

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June 2, 1992

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT Distribution unlimited.
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of New Orleans 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) University of New Orleans New Orleans, LA 70148	7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-91-J-1758
8c. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Luminescent Nitro Derivatives of Benzotriazolo[2,1-a]benzotriazole

12. PERSONAL AUTHOR(S)
Q. Lu and J. H. Boyer

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	June 2, 1992	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Nitro compounds, triazolotriazoles, fluorescence, laser activity.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

See attached

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
[X] UNCLASSIFIED/UNLIMITED [ ] SAME AS RPT. [ ] OTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Joseph H. Boyer	22b. TELEPHONE (Include Area Code) (504)286-7225
	22c. OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

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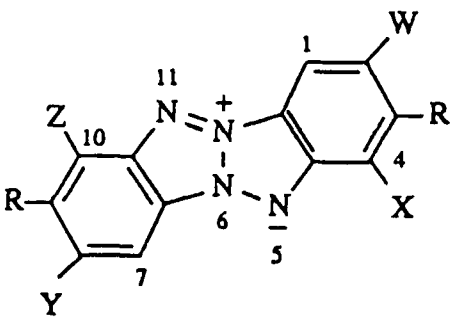
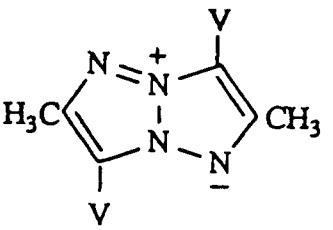
Fluorescence was enhanced and laser activity introduced by substitution in 5,11-dehydro-5H,11H-benzotriazolo[2,1-*a*]benzotriazole **6** to give 2-nitro, 2,8-dinitro, 2,4,8-trinitro, and 2,4,8,10-tetranitro derivatives **9a–d**. Luminescence for compounds **6**, **9a–d**, and the 2,8-dinitro-3,9-dimethyl and 2,3,8,9-tetramethyl-4,10-dinitro derivatives **11a,b** was erratically solvent dependent when examined in ethyl acetate, acetonitrile, and acetone, and was most efficient in the 2,8-dinitro derivative **9b**, [λ_f 479 nm (ethyl acetate) Φ 0.98, λ_f 501 nm (acetonitrile) Φ 0.58, and λ_f 494 nm (acetone) Φ 0.61] and in the tetranitro derivative **9d** [λ_f 509 nm (acetonitrile) Φ 0.81 and λ_f 511 nm (acetone) Φ 0.66]. With laser activity at 560–590 nm (acetonitrile) the dye **9b** was 30 percent as efficient as rhodamine 6G (ethanol) in power output. Luminescence was quenched by the reduction of nitro groups to give 2-amino and 2,8-diamino derivatives **9e,f** and by the conversion of the tetranitro compound **9d** to an unassigned diazido dinitro derivative **9g**. Luminescence was not detected in 2,5-dimethyl-3,6-dinitro-1,3a,4,6a-tetraazapentalene **14** and ethyl 2,5-dimethyl-1,3a,4,6a-tetraazapentalene-3,6-dicarboxylate **15**. Azidoazobenzenes were obtained from 4-methyl- and 4,5-dimethyl-1,2-phenylene diamines via oxidation with lead dioxide to aminoazobenzene derivatives followed by treatment of the diazotized amines with sodium azide and thermolysis of azido intermediates to give 3,9-dimethyl and 2,3,8,9-tetramethyl derivatives **10 a,b** of the triazolotriazole **6**. Nitration converted the triazole **6** to the 2,4,8-trinitro derivative **9c** and the alkyltriazoles to their dinitro derivatives **11 a,b**.





14 V = NO_2

15 V = $CO_2CH_2CH_3$

6 W = X = Y = Z = R = H

9a W = NO_2, X = Y = Z = R = H

9b W = Y = NO_2, X = Z = R = H

9c W = X = Y = NO_2, Z = R = H

9d W = X = Y = Z = NO_2, R = H

9e W = NH_2, X = Y = Z = R = H

9f W = Y = NH_2, X = Z = R = H

9g unassigned diazidodinitro derivative

10a W = X = Y = Z = H, R = CH_3

10b W = R = Y = CH_3, X = Z = H

11a W = Y = NO_2, X = Z = H, R = CH_3

11b W = Y = R = CH_3, X = Z = NO_2